

PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY



(Chapter II of the Patent Cooperation Treaty)

(PCT Article 36 and Rule 70)

REC'D 30 AUG 2005

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Applicant's or agent's file reference 63104A	FOR FURTHER ACTION See Form PCT/PEA/416	
International application No. PCT/US2004/012246	International filing date (day/month/year) 22.04.2004	Priority date (day/month/year) 25.04.2003
International Patent Classification (IPC) or national classification and IPC C07C67/347, C07C69/716, C07C69/738, C07C67/31, C07C69/675, C07C69/732, C11C3/00, C11C3/12		
Applicant DOW GLOBAL TECHNOLOGIES INC. et al.		
<p>1. This report is the international preliminary examination report, established by this International Preliminary Examining Authority under Article 35 and transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of 6 sheets, including this cover sheet.</p> <p>3. This report is also accompanied by ANNEXES, comprising:</p> <p>a. <input checked="" type="checkbox"/> sent to the applicant and to the International Bureau a total of 6 sheets, as follows:</p> <p><input type="checkbox"/> sheets of the description, claims and/or drawings which have been amended and are the basis of this report and/or sheets containing rectifications authorized by this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions).</p> <p><input type="checkbox"/> sheets which supersede earlier sheets, but which this Authority considers contain an amendment that goes beyond the disclosure in the international application as filed, as indicated in item 4 of Box No. I and the Supplemental Box.</p> <p>b. <input type="checkbox"/> (sent to the International Bureau only) a total of (indicate type and number of electronic carrier(s)) , containing a sequence listing and/or tables related thereto, in computer readable form only, as indicated in the Supplemental Box Relating to Sequence Listing (see Section 802 of the Administrative Instructions).</p>		
<p>4. This report contains indications relating to the following items:</p> <p><input checked="" type="checkbox"/> Box No. I Basis of the opinion</p> <p><input type="checkbox"/> Box No. II Priority</p> <p><input type="checkbox"/> Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability</p> <p><input type="checkbox"/> Box No. IV Lack of unity of invention</p> <p><input checked="" type="checkbox"/> Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement</p> <p><input type="checkbox"/> Box No. VI Certain documents cited</p> <p><input type="checkbox"/> Box No. VII Certain defects in the international application</p> <p><input type="checkbox"/> Box No. VIII Certain observations on the international application</p>		
Date of submission of the demand 22.02.2005	Date of completion of this report 26.08.2005	
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized Officer Seelmann, M Telephone No. +49 89 2399-8335 	

**INTERNATIONAL PRELIMINARY REPORT
ON PATENTABILITY**

International application No.
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Box No. I Basis of the report

1. With regard to the **language**, this report is based on the international application in the language in which it was filed, unless otherwise indicated under this item.
- ☐ This report is based on translations from the original language into the following language , which is the language of a translation furnished for the purposes of:
- ☐ international search (under Rules 12.3 and 23.1(b))
 - ☐ publication of the international application (under Rule 12.4)
 - ☐ international preliminary examination (under Rules 55.2 and/or 55.3)
2. With regard to the **elements*** of the international application, this report is based on *(replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report):*

Description, Pages

1-26 as originally filed

Claims, Numbers

1-34 received on 24.02.2005 with letter of 22.02.2005

Drawings, Sheets

1/1 as originally filed

- ☐ a sequence listing and/or any related table(s) - see Supplemental Box Relating to Sequence Listing
3. ☐ The amendments have resulted in the cancellation of:
- ☐ the description, pages
 - ☐ the claims, Nos.
 - ☐ the drawings, sheets/figs
 - ☐ the sequence listing (*specify*):
 - ☐ any table(s) related to sequence listing (*specify*):
4. ☐ This report has been established as if (some of) the amendments annexed to this report and listed below had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).
- ☐ the description, pages
 - ☐ the claims, Nos.
 - ☐ the drawings, sheets/figs
 - ☐ the sequence listing (*specify*):
 - ☐ any table(s) related to sequence listing (*specify*):

* If item 4 applies, some or all of these sheets may be marked "superseded."

**INTERNATIONAL PRELIMINARY REPORT
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Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes: Claims	1-34
	No: Claims	
Inventive step (IS)	Yes: Claims	
	No: Claims	1-34
Industrial applicability (IA)	Yes: Claims	1-34
	No: Claims	

2. Citations and explanations (Rule 70.7):

see separate sheet

**INTERNATIONAL PRELIMINARY
REPORT ON PATENTABILITY
(SEPARATE SHEET)**

International application No.

PCT/US2004/012246

- D1** US 3 787 459 cited in the application
D2 EP 0 711 748 cited in the application
D3 US 5 756 854

The present application pretains to a certain aldehyde composition (claims 1-11) and preparation thereof (claims 12-17) as well as a certain alcohol composition (claims 18-25) and preparation thereof (claims 26-34).

Item V

Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

V.1 Amendments - Art.34(2)b) PCT

Claims 18, 21, 24 and 26 were amended. In particular the dependency of claim 24 was corrected (Rule 91.1b) PCT). The alcohol composition of claims 18, 26 and 21 was restricted to a diol/triol weight ratio of greater than 5/1 and 8/1 respectively. All these amendments satisfy the requirements of article 34(2)b) PCT.

V.2 Novelty - Art.33(2) PCT

Hydroformylation of fatty acid esters and/or with subsequent reduction to the corresponding hydroxymethyl products is known from the prior art documents **D1** to **D3**.

The aldehyde composition disclosed in example 20 of **D1** comprises 38.1 to 12.4 weight % of monoformyl and 50.0 to 85.4 weight % of di-/triformyl depending of the number of hours of the hydroformylation reaction (table V). The exact ratio of diformyl and triformyl is not provided. In this document starting from safflower oil methyl esters only monoformyl and diformyl products are detected (examples 21-22, table VI).

The aldehyde composition of **D2** in example 6 comprises 39 weight-% of monoformyl, 17 weight-% of diformyl and 5 weight-% of triformyl, which provides a weight ratio diformyl to triformyl of 3.4. Such composition is said to be further reduced with hydrogen in the presence of a Raney-Nickel as catalyst. So the disclosure of an alcohol composition with mono-, di- and trialcohol in the weight-% provided in claim 18 is implicitly given in this document but for a diol/triol weigh ratio lower than 5/1.

The aldehyde composition of **D3** comprises also monoformyl, diformyl and triformyl products but with a diformyl to triformyl ratio lying between 0.3 and 1.5.

The aldehyde and alcohol compositions of the present application differs from the above-cited documents in that the weight ratio of diformyl to triformyl is greater than 5 ! Novelty is accordingly recognized for the subject-matters of claims 1, 12, 18 and 26 as well as their dependent claims.

V.2 Inventive step - Art.33(3) PCT

The closest related aldehyde composition of **D2** differs from the present one in that the diformyl to triformyl weight ratio is of 3.4 and not greater than 5. The technical problem posed is to provide an alcohol/aldehyde composition derivable from seed oils and convertible to polyols having acceptable properties for use in polyurethane slab stock flexible foams. In the examples of the present application, aldehyde compositions were prepared fulfilling the requirements of claim 1. A test report was provided by the applicant in his letter of 22.02.2005 showing that the obtained alcohol composition, from the corresponding aldehyde composition upon reduction, can be converted into polyols for use in the production of flexible polyurethane foams. The proposed aldehyde/alcohol compositions solve the technical problem posed. Nevertheless the proposed solution could only be seen as a simple alternative, since the aldehyde/alcohol composition is also derivable from a seed oil in **D2** and differs simply by the amount of diformyl and triformyl present. A man skilled in the art would not foreseen that the modification of 1.5 in this ratio influences the properties of the final polyurethanes. Therefore in order for an inventive step to be recognized, comparative data are necessary to prove a surprising effect in view of an increase in the weight ratio of diformyl towards triformyl. No inventive step can be recognized for the different subject-matters of claims 1-34.

V.3 Further comments:

- 3.1 The use of the word "about" especially in connection with numerical ranges is generally regarded as rendering the determination of the exact scope of the range difficult. When used in a claim, this results in a lack of clarity, contrary to Article 6 PCT.
- 3.2 Claims 8 and 25 are formulated as "product-by-process" claims. The specific

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conditions required to recover such an aldehyde/alcohol composition should be introduced in these claims in agreement with the Guidelines II - 5.26 / 5.27 PCT.

- 3.3 The expression "incorporated herein by reference" should have been removed from the description in each of its occurrence according to the Guidelines II - 4.26 PCT.
- 3.4 The term expression " or the like" is indefinite and should have therefore been removed from the description (Guidelines II - 4.31 PCT).

AMENDED CLAIMS (MARKED-UP VERSION)

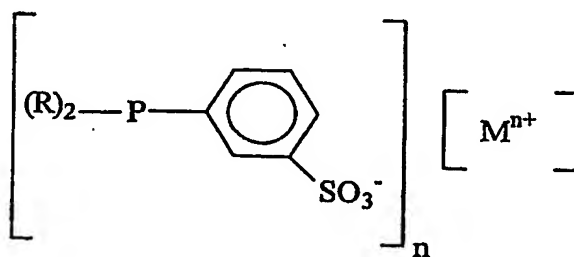
1. An aldehyde composition comprising a mixture of formyl-substituted fatty acids or fatty acid esters comprising in terms of formyl distribution from greater than about
5 10 to less than about 95 percent monoformyl, from greater than about 1 to less than about 65 percent diformyl, from greater than about 0.1 to less than about 10 percent triformyl by weight, based on the total weight of the composition, and further comprising a diformyl to triformyl weight ratio of greater than about 5/1.
2. The aldehyde composition of Claim 1 further comprising from greater
10 than about 3 to less than about 20 percent saturates, by weight.
3. The aldehyde composition of Claim 1 or 2 further comprising from greater than about 1 to less than about 20 percent unsaturates, by weight.
4. The aldehyde composition of Claim 1 wherein the diformyl to triformyl weight ratio is greater than about 10/1.
- 15 5. The aldehyde composition of Claim 1 comprising less than about 10 weight percent total heavies impurities.
6. The aldehyde composition of Claim 1 comprising from greater than about 25 to less than about 45 percent monoformyl, from greater than about 20 to less than about 50 percent diformyl, and from greater than about 0.5 to less than about 5 percent triformyl
20 substituted fatty acids or fatty acid esters, by weight.
7. The aldehyde composition of Claim 1 comprising from greater than about 30 to less than about 40 percent monoformyl, from greater than about 25 to less than about 45 percent diformyl, and from greater than about 1 to less than about 2.6 percent triformyl substituted fatty acids or fatty acid esters, by weight.
- 25 8. The aldehyde composition of Claim 1 being prepared by a process comprising contacting a mixture of unsaturated fatty acids or fatty acid esters with carbon monoxide and hydrogen in the presence of a Group VIII transition metal-organophosphine metal salt ligand complex catalyst, and optionally free organophosphine metal salt ligand, under process conditions sufficient to convert greater than about 80 weight percent of
30 unsaturated fatty acids or fatty acid esters to monoformyl products.
9. The composition of Claim 8 wherein the mixture of unsaturated fatty acids or fatty acid esters is derived from a seed oil.

10. The composition of Claim 8 wherein the seed oil is selected from naturally occurring and genetically modified seed oils of the group consisting of castor, soybean, olive, peanut, rapeseed, corn, sesame, cottonseed, canola, safflower, linseed, sunflower, including high oleic oils, and mixtures thereof.

11. The composition of Claim 8 wherein the temperature is greater than about 45°C and less than about 200°C, and wherein the total pressure is greater than about 1 psia (6.9 kPa) and less than about 10,000 psia (69 MPa).

12. A process of preparing an aldehyde composition comprising contacting a mixture of unsaturated fatty acids or fatty acid esters with carbon monoxide and hydrogen in the presence of a Group VIII transition metal-organophosphine metal salt ligand complex catalyst, and optionally free organophosphine metal salt ligand, under process conditions sufficient to hydroformylate greater than about 80 weight percent of the unsaturated fatty acids or fatty acid esters to monoformyl products, so as to produce a mixture of formyl-substituted fatty acids or fatty acid esters comprising in terms of formyl distribution from greater than about 10 to less than about 95 percent monoformyl, from greater than about 1 to less than about 65 percent diformyl, and from greater than about 0.1 to less than 10 percent triformyl by weight, based on the total weight of the composition, and having a diformyl to triformyl weight ratio of greater than about 5/1.

13. The process of Claim 12 wherein the ligand is a monosulfonated tertiary organophosphine represented by the following formula:



wherein each R group individually represents a radical containing from 1 to about 30 carbon atoms; wherein M represents a metal cation selected from the group consisting of alkali and alkaline earth metals; and wherein n has a value of 1 or 2 corresponding to the valence of the particular metal cation M.

14. The process of Claim 13 wherein the ligand is selected from the group consisting of the monosulfonated metal salts of triphenylphosphine, diphenylcyclohexylphosphine, phenyldicyclohexylphosphine, tricyclohexylphosphine, diphenylisopropylphosphine, phenyldiisopropylphosphine, diphenyl-t-butylphosphine, phenyldi-t-butylphosphine, and mixtures thereof.

15. The process of Claim 12 wherein the Group VIII transition metal of the complex catalyst is selected from rhodium, ruthenium, cobalt, iridium, and mixtures thereof.

16. The process of Claim 12 wherein the temperature is greater than about 45°C and less than about 200°C, and wherein the total pressure is greater than about 1 psia (6.9 kPa) and less than about 10,000 psia (69 MPa).

17. The process of Claim 12 wherein the carbon monoxide partial pressure is greater than about 1 psia and less than about 250 psia; and wherein the hydrogen partial pressure is greater than about 10 psia and less than about 250 psia.

18. An alcohol composition comprising a mixture of hydroxymethyl-substituted fatty acids or fatty acid esters comprising in terms of hydroxy distribution from greater than about 10 to less than about 95 percent mono alcohol, from greater than about 1 to less than about 65 percent diol, and from greater than about 0.1 to less than about 10 percent triol by weight, based on the total weight of the composition, and further having a diol to triol weight ratio of greater than 5/1. (Support, specification at page 8, lines 16-18)

19. The alcohol composition of Claim 18 further comprising from greater than about 3 to less than about 35 percent saturates.

20. The alcohol composition of Claim 18 or 19 further comprising from greater than about 0 to less than about 10 percent unsaturates.

21. The alcohol composition of Claim 18 having a diol to triol weight ratio of greater than about ~~2.5/1~~ 8/1. (Support, specification at page 8, lines 16-18)

22. The alcohol composition of Claim 18 comprising less than about 10 weight percent total impurities selected from the group consisting of lactols, lactones, saturated cyclic ethers, unsaturated cyclic ethers, and heavies.

23. The alcohol composition of Claim 18 comprising from greater than about 25 to less than about 70 percent monoalcohol, from greater than about 20 to less than about

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50 percent diol, and from greater than about 0.5 to less than about 5 percent triol substituted fatty acids or fatty acid esters, by weight.

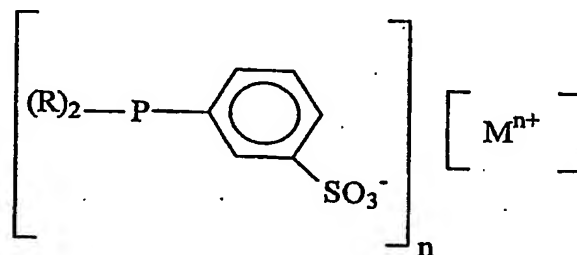
24. The alcohol composition of ~~Claim 17~~ Claim 18 comprising from greater than about 30 to less than about 45 percent monoalcohol, from greater than about 25 to less than about 45 percent diol, and from greater than about 1 to less than about 4 percent triol substituted fatty acids or fatty acid esters, by weight. (Correction of inadvertent typographical error)

25. The alcohol composition of Claim 18 being prepared by a process comprising (a) contacting a mixture comprising unsaturated fatty acids or fatty acid esters with carbon monoxide and hydrogen in the presence of a Group VIII transition metal-organophosphine metal salt ligand complex catalyst, and optionally, free organophosphine metal salt ligand, under conditions sufficient to hydroformylate greater than about 80 weight percent of the unsaturated fatty acids or fatty acid esters to monoformyl products, so as to obtain a hydroformylation reaction mixture comprising an aldehyde composition of formyl-substituted fatty acids or fatty acid esters; (b) separating the aldehyde composition from the hydroformylation reaction mixture; and thereafter (c) hydrogenating the aldehyde composition with a source of hydrogen in the presence of a hydrogenation catalyst under process conditions sufficient to obtain the alcohol composition.

26. A process of preparing an alcohol composition comprising (a) contacting a mixture comprising unsaturated fatty acids or fatty acid esters with carbon monoxide and hydrogen in the presence of a Group VIII transition metal-organophosphine metal salt ligand complex catalyst, and optionally, free organophosphine metal salt ligand, under conditions sufficient to hydroformylate greater than about 80 weight percent of unsaturated fatty acids or fatty acid esters to monoformyl products, so as to obtain a hydroformylation reaction mixture comprising an aldehyde product of formyl-substituted fatty acids or fatty acid esters; (b) separating the aldehyde product from the hydroformylation reaction mixture; and thereafter (c) hydrogenating the aldehyde product with a source of hydrogen in the presence of a hydrogenation catalyst under process conditions sufficient to obtain the alcohol composition comprising a mixture of hydroxymethyl-substituted fatty acids or fatty acid esters comprising in terms of hydroxy distribution from greater than about 10 to less than about 95 percent mono alcohol, from greater than about 1 to less than about 65 percent diol, and from greater than about 0.1 to less than about 10 percent triol by weight, based on the

total weight of the composition, and further having a diol to triol weight ratio of greater than 5/1. (Support, specification at page 8, lines 16-18)

27. The process of Claim 26 wherein the ligand is a monosulfonated tertiary organophosphine represented by the following formula:



wherein each R group individually represents a radical containing from 1 to about 30 carbon atoms; wherein M represents a metal cation selected from the group consisting of alkali and alkaline earth metals; and wherein n has a value of 1 or 2 corresponding to the valence of the particular metal cation M.

28. The process of Claim 27 wherein the ligand is selected from the group consisting of the monosulfonated salts of triphenylphosphine, diphenylcyclohexylphosphine, phenyldicyclohexylphosphine, tricyclohexylphosphine, diphenylisopropylphosphine, phenyldiisopropylphosphine, diphenyl-t-butylphosphine, phenyl-di-t-butylphosphine, and mixtures thereof.

29. The process of Claim 26 wherein the Group VIII transition metal is selected from rhodium, ruthenium, cobalt, iridium, and mixtures thereof.

30. The process of Claim 26 wherein the hydroformylation is conducted at a temperature of greater than about 45°C and less than about 200°C and a total pressure greater than about 1 psia (6.9 kPa) and less than about 10,000 psia (69 MPa).

31. The process of Claim 26 wherein the aldehyde composition is separated from the hydroformylation reaction mixture by extraction.

32. The process of Claim 26 wherein the hydrogenation catalyst comprises a metal selected from the group consisting of Group VIII, Group I, and Group II metals and mixtures thereof.

33. The process of Claim 32 wherein the hydrogenation catalyst comprises Raney nickel or supported nickel.

34. The process of Claim 26 wherein the hydrogenation is conducted at a temperature greater than about 50°C and less than about 250°C and at a pressure greater than
5 about 50 psig (345 kPa) and less than about 1,000 psia (6,895 kPa).